

November 24, 1892.

Sir JOHN EVANS, K.C.B., Vice-President and Treasurer, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the list of Officers and Council nominated for election was read as follows:—

*President*.—The Lord Kelvin, D.C.L., LL.D.

*Treasurer*.—Sir John Evans, K.C.B., D.C.L., LL.D.

*Secretaries*.—{ Professor Michael Foster, M.A., M.D.  
The Lord Rayleigh, M.A., D.C.L.

*Foreign Secretary*.—Sir Archibald Geikie, LL.D.

*Other Members of the Council*.—Captain William de Wiveleslie Abney, C.B.; Sir Benjamin Baker, K.C.M.G., LL.D.; Professor Isaac Bayley Balfour, M.A.; William Thomas Blanford, F.G.S.; Professor George Carey Foster, B.A.; Richard Tetley Glazebrook, M.A.; Frederick Ducane Godman, F.L.S.; John Hopkinson, D.Sc.; Professor Joseph Norman Lockyer, F.R.A.S.; Professor John Gray McKendrick, M.D.; William Davidson Niven, M.A.; William Henry Perkin, LL.D.; Rev. Professor B. Price, D.D.; the Marquis of Salisbury, K.G., M.A.; Adam Sedgwick, M.A.; Professor William Augustus Tilden, D.Sc.

The following Papers were read:—

I. "Ionic Velocities." By W. C. DAMPIER WHETHAM, B.A., Fellow of Trinity College, Cambridge. Communicated by J. J. THOMSON, F.R.S. Received October 19, 1892.

(Abstract.)

In order to explain the fact that during the electrolysis of a salt solution the ions into which the salt is divided only appear at the electrodes, the intervening solution being unaltered, we must suppose that the ions travel in opposite directions through the liquid. Kohl-

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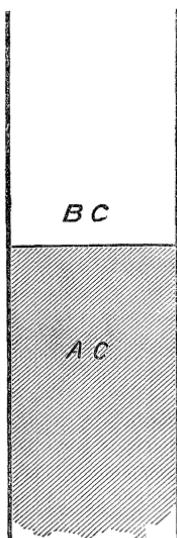
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Kohlrausch, from the results of a series of experiments on the conductivities of salt solutions, concluded that each ion travelled through dilute solutions with a definite speed when urged forward by a definite potential gradient, independently of the other ion present, and introduced the idea of specific ionic velocity. He calculated the value of this velocity for many substances, using his own conductivity measurements to give the arithmetical sum of the opposite ionic velocities, and Hittorf's "migration" data to give their ratio. From these values of the velocities he worked out the conductivity of many salt solutions, and the agreement with observation of the results so obtained furnished the first confirmation of the theory.

Dr. Oliver Lodge actually observed the velocity of the hydrogen ion as it travelled along a tube containing sodium chloride dissolved in a weak jelly, decolorising phenol-phthalein as it went. He obtained the numbers 0.0029, 0.0026, and 0.0024 cm. per sec. as the velocity of the hydrogen ion under a potential gradient of 1 volt per cm., while Kohlrausch gives 0.0030.

This close agreement led me to undertake a series of experiments in order to find a method of determining ionic velocities which would work under more reliable conditions. Consider the boundary

FIG. 1.

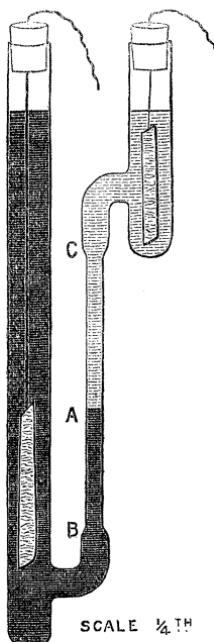


of two salt solutions of slightly different density which have one ion in common, but are of different colours (fig. 1). Let us denote the salts by AC and BC. When a current passes across the boundary

there will be a transference of C ions in one direction and of A and B ions in the other. If A and B are the kations, the colour boundary will move with the current, and its velocity will, in any case, indicate the velocity of the ion causing the change in colour.

The apparatus used (fig. 2) consisted of two vertical glass tubes

FIG. 2.



about 2 cm. in diameter, joined by a third considerably narrower, which was bent parallel to the others for the greater part of its length. The longer tube was filled with the denser solution to about the level A, and then the lighter solution was run into the other tube from a burette till it just began to trickle over the shoulder and run down to A. The proper solutions were then run into the two limbs at rates just sufficient to keep the junction at rest. The current was passed from platinum electrodes which could be connected with a battery of twenty-six accumulators by means of platinum wires. The corks fitted loosely to allow any gas which might be evolved to escape.

The junction tube had an effective length of 13·8 cm., which, divided into the total difference of potential, gave the potential gradient. The correction due to changes of density produced by the passage of the current can be shown to be quite negligible.

When the solutions are of different specific resistance, there will be a discontinuity of potential gradient at the boundary and a consequent electrification. This can be got rid of entirely by using solutions of the same specific resistance, and in all cases the effect on the velocity of the boundary is non-reversible, and can be approximately eliminated by reversing the current and taking the mean value of the velocity. If the velocity is found to be the same in opposite directions when the current is reversed, the effect must be negligible.

The first solutions used were those of copper and ammonium chlorides dissolved in aqueous ammonia. The copper solution is a deep blue; the other colourless. Their strength was 0·18 gram-equivalent per litre. The mean velocity when the current was passing upward came out 0·0406 cm. per minute, and when passing downwards 0·0441 cm. per minute. In each case the junction moved with the current. The potential gradient was 2·73 volts per cm., which gives as the specific ionic velocity

$$0\cdot00026 \text{ cm. a second.}$$

Kohlrausch gives for infinite dilution

$$0\cdot00031 \text{ cm. a second.}$$

Solutions of potassium permanganate and potassium chloride were taken to show the motion of the acid radicles, and, as it should, the junction moved *against* the current. If we assume that the disappearance of the red colour can only occur where permanganate is replaced by chloride, the motion of the junction can be taken as an indication of the velocity of chlorine. The result for solutions of 0·046 gram-equivalent per litre was 0·00057 cm. per sec., and for solutions of about one-tenth this strength 0·00059 cm. per sec. Kohlrausch gives 0·00053 cm. per sec. as the specific ionic velocity of chlorine.

The success of these preliminary experiments led me to attempt to improve the method. I investigated one pair of salts with exactly the same specific resistance for the same strength, though in cases where this condition is nearly fulfilled (such as that of copper and ammonium chlorides), the error thus introduced can be shown to be negligible.

The direct estimation of the potential gradient is unsatisfactory, but if we measure the specific resistance of the solution ( $r$ ), the area of the junction tube ( $A$ ), and the current ( $\gamma$ ), we can calculate the specific ionic velocity ( $v_i$ ) from the observed velocity of the boundary ( $v$ ), for it is easy to show that

$$v_i = \frac{vA}{\gamma r}.$$

This method was used to repeat the copper determination, using solutions whose strength was 0·1 gram-equivalent per litre. The specific resistances of the copper and ammonium chlorides were measured by Fitzpatrick's method, and came out  $157 \times 10^9$  and  $117 \times 10^9$  in C.G.S. units respectively. The current was measured by passing it through a previously graduated galvanometer. The velocity of the junction was determined by reading its position at different times by means of a kathetometer.

When the current was passing upwards, the upward velocity was  
 $1\cdot70, 1\cdot60, 1\cdot53, 1\cdot43$  cm. per hour; mean,  $1\cdot57$  cm. per hour,  
and when it was passing downwards, the downward velocity was  
 $1\cdot45, 1\cdot65, 1\cdot70$  cm. per hour; mean,  $1\cdot60$  cm. per hour.

This gives a specific ionic velocity in solutions of 0·1 gram-equivalent of

$$0\cdot000309 \text{ cm. per sec.}$$

as compared with Kohlrausch's number for solutions of infinite dilution,

$$0\cdot00031 \text{ cm. per sec.}$$

Solutions of potassium bichromate and potassium carbonate have specific resistances which are very nearly indeed (within 3 per cent.) the same for the same strengths, and a solution of carbonate was adjusted in strength till even this small difference between it and a 0·1 solution of bichromate was much reduced.

The first point I investigated with these solutions was the influence of change of potential gradient on the velocity. These should, on Kohlrausch's theory, obviously be proportional to each other.

At first, all the cells available were used. The velocity of the junction when the current passed downwards was

$3\cdot63, 3\cdot39, 3\cdot65, 3\cdot24$  cm. per hour; mean,  $3\cdot48$  cm. per hour  
in an upward direction.

When the current was sent upward the velocity was downwards and came out

$$3\cdot28, 3\cdot55, 3\cdot45 \text{ cm. per hour; mean, } 3\cdot43 \text{ cm. per hour.}$$

$$\text{This gives } v_1 = 0\cdot00048 \text{ cm. per sec.}$$

An E.M.F. of about one-third that used above was then applied.

$$\begin{aligned} \text{Mean downward velocity, } & 1\cdot44 \text{ cm. per hour.} \\ \text{, , upward } & 1\cdot29 \text{ cm. per hour.} \\ v_1 = & 0\cdot00047 \text{ cm. per sec.} \end{aligned}$$

Thus the value obtained for the specific ionic velocity is independent of the E.M.F. applied, or *the velocity of the ions is proportional to the potential gradient.*

The experiments with the large E.M.F. were repeated with new solutions—

$$v_1 = 0.00046 \text{ cm. per sec.}$$

The specific velocity of the bichromate group is not given by Kohlrausch, but can at once be calculated by his method from a knowledge of the molecular conductivity ( $9.10 \times 10^{-12}$ ), which was determined by Lenz, and of the migration constant, which was given by Hittorf as 0.502. The velocity comes out

$$v_1 = 0.000473,$$

a number identical with the mean value of the measurements described above.

In order to estimate the effect of a discontinuity of potential gradient, another determination of the velocity of this same ion was then made, the carbonate being replaced by potassium chloride, whose conductivity is considerably greater than that of the bichromate ( $11.13 \times 10^{-12}$  and  $9.10 \times 10^{-12}$ ). Two experiments were made :—

$$\begin{array}{ll} \text{(i.) Upward velocity . . . .} & v_1 = 0.000516 \\ \text{Downward velocity ..} & 0.000394 \end{array} \left. \right\} v_1 = 0.000455.$$

$$\begin{array}{ll} \text{(ii.) Upward velocity . . . .} & v_1 = 0.000483 \\ \text{Downward velocity ..} & 0.000402 \end{array} \left. \right\} v_1 = 0.000443.$$

These numbers show that the effect is to increase the velocity in one direction, and to diminish it in the other, while (at all events, if the difference of specific resistance is not great) the mean value gives a fair approximation to that obtained when solutions of identical conductivity are used.

With solutions of different resistances, the junction is often observed to become sharp when travelling in one direction, and vague when travelling in the other. This is owing to the fact that any ion which gets separated from the main body finds itself in a region where the potential gradient is different. Its velocity is therefore altered, and in the first case it rejoins the ranks, and in the second it gets further and further separated from them.

The investigation was also extended to the case of alcoholic solutions. These possess a very much less conductivity than the corresponding aqueous ones, and the question whether Kohlrausch's theory still held good seemed of great interest. No data for the migration constants are known ; hence a modification of the method was applied. An experimental measurement of the velocities of both ions of some

salt was made, and their sum compared with the value deduced from the conductivity.

The first salt used was cobalt chloride, the alcoholic solution of which is of a deep blue colour. The velocity of the chlorine ion was measured by setting up the cobalt chloride with cobalt nitrate, the colour of which is red, and that of the cobalt by a cobalt chloride and calcium chloride pair, the latter salt being colourless.

Some little difficulty was encountered in getting solutions of convenient strength. If very weak, the colours were not easily seen, while, if the strength approached 0·1 gram-equivalent per litre, irregularities of behaviour appeared. Finally, solutions of 0·05 gram-equivalent were used, but even here the effects of too great concentration were still appreciable.

Chlorine.....	$v_1 = 0\cdot000026$
Cobalt.....	$0\cdot000022$
The sum is.....	$U = 0\cdot000048$

This can be calculated from the conductivity ( $2\cdot86 \times 10^{-13}$ ), and comes out

$$U = 0\cdot000060.$$

Cobalt nitrate was then investigated. Its conductivity is greater than that of the chloride ( $3\cdot80 \times 10^{-13}$ ), which leads us to expect that its behaviour will be normal at concentrations greater than those at which the chloride becomes irregular. Such was found to be the case. We should also suppose that its agreement with theory will be closer. The pairs used were cobalt nitrate—cobalt chloride and cobalt nitrate—calcium nitrate.

Nitrate group ( $\text{NO}_3$ ).....	$v_1 = 0\cdot000035$
Cobalt.....	$v_1 = 0\cdot000044$

The sum of these is

$$U = 0\cdot000079.$$

The value calculated from the conductivity is

$$U = 0\cdot000079.$$

The explanation of the irregularities observed in strong solutions is most easily found by the supposition that complex ions are formed as the strength increases. The further discussion of this point is postponed till some more experiments I am making are ready for publication.

A table of results is appended :—

## Specific Ionic Velocities.

## I. Aqueous Solutions.

Ion.	Velocity observed.	Velocity calculated from Kohlrausch's theory.
Copper .....	0·00026* 0·000309	0·00031
Chlorine .....	0·00057* 0·00059*	0·00053
Bichromate group (Cr <sub>2</sub> O <sub>7</sub> )	0·00048 0·00047 0·00046	0·000473

## II. Alcoholic Solutions.

Salt.	Velocity of anion (observed).	Velocity of cation (observed).	Sum of velocities (observed).	Sum of velocities (calculated).
Cobalt chloride .....	0·000026	0·000022	0·000048	0·000060
Cobalt nitrate .....	0·000035	0·000044	0·000079	0·000079

## II. "Memoir on the Theory of the Compositions of Numbers."

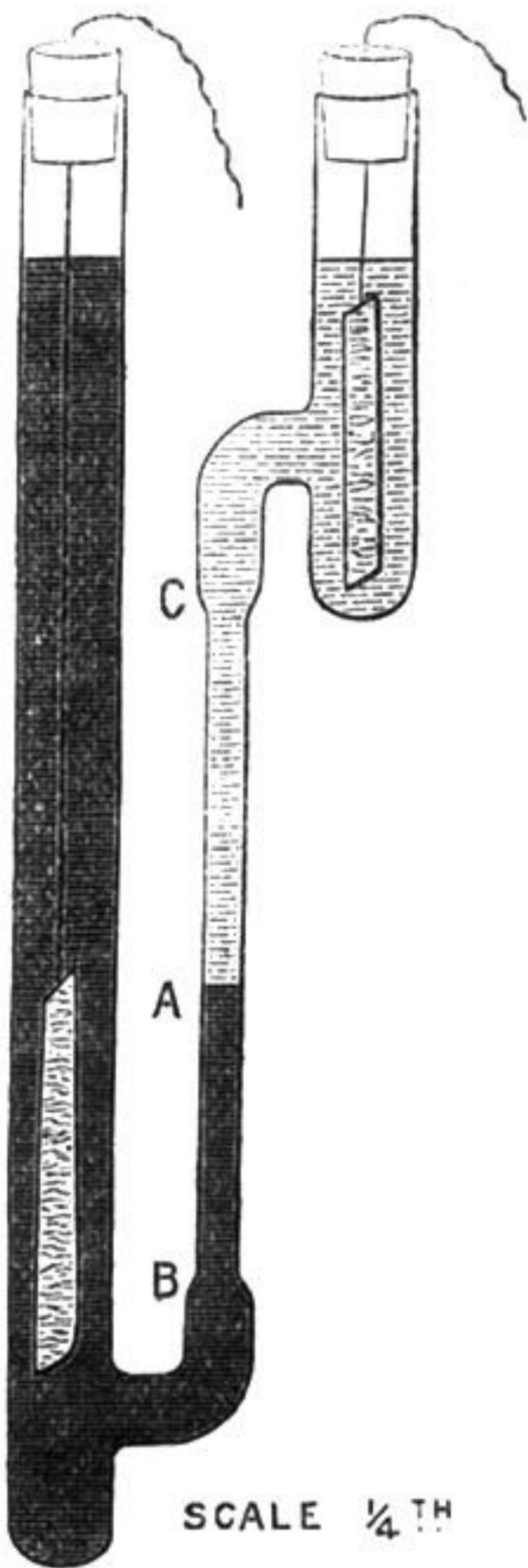
By P. A. MACMAHON, Major R.A., F.R.S. Received November 17, 1892.

## (Abstract.)

In the theory of the partitions of numbers the order of occurrence of the parts is immaterial. Compositions of numbers are merely partitions in which the order of the parts is essential. In the nomenclature I have followed H. J. S. Smith and J. W. L. Glaisher. What are called "unipartite" numbers are such as may be taken to enumerate undistinguished objects. "Multipartite" numbers enumerate objects which are distinguished from one another to any given extent; and the objects are appropriately enumerated by an ordered assemblage of integers, each integer being a unipartite number which specifies the number of objects of a particular kind; and such assemblage constitutes a multipartite number. The 1st

\* Preliminary determinations.

FIG. 2.



SCALE  $\frac{1}{4}$  TH